Polymer-copper complexes as homogeneous redox catalysts

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SUMMARY

This thesis presents an investigation into the application of polymer-attached catalytically active sites as immobilized homogeneous redox catalysts. A particularly interesting feature in this respect, i.e. the capability of the macromolecular chain itself to influence the catalytic behaviour of the attached sites rather than to act as an inert carrier (see sections I.1, I.2 and I.3), was considered in detail in chapters V and VI.

The optimal immobilization method seems to involve the utilization of linear macromolecules, which are linked by the terminal monomer unit to a solid support as indicated in Fig. 1.1,since this method preserves the homogeneous character on a local scale. In this study kinetic experiments were performed using soluble linear counterparts, which have locally a similar adaptability.

Oxidative coupling reactions, catalyzed by copper complexes with polymer-attached tertiary amines, proved to be suitable model systems for investigating macromolecular catalysis as outlined in section II.3. One of these model reactions, i.e. the oxidative coupling of 2,6-dimethylphenol, involves two destinct reaction paths as represented in Fig. 2.6, which also permitted the investigation of influences on catalytic specificity.

Macromolecular amine ligands were synthesized by modification of non-functional polymers (section II.1.1) or by (co-)polymerization of functional monomers (section II.1.2). The latter method offered the advantages of better regulation of the degree of functionalization, α, and exclusion of undesirable cross-linking side reactions. This permitted the preparation of macromolecular ligands over the entire α range.

The nature of the catalytically active sites has been investigated in chapter III by X-ray diffraction (III.2), spectroscopic methods (III.3) and kinetic experiments (III.4), utilizing a suitable low molecular weight model complex, i.e. a copper complex with the bidentate N,N,N',N'-tetramethylethane-1,2-diamine, TMED, viz. $\{TMED.Cu(OH)_2Cu.TMED\}Cl_2$. It appeared that two distinct binuclear copper/TMED complexes could be synthesized, depending on the preparation method as visualized in Fig. 3.1. The chloro-bridged complex was found to be only slightly active and to yield specifically the C-C-coupled dimer product in the oxidative coupling of 2,6-dimethylphenol, i.e. the so-called "diphenoquinone", DPQ. On the other hand, the hydroxo-bridged counterpart exhibited a much higher catalytic activity in producing mainly the C-O-coupled polymer product, poly-2,6-dimethyl-1,4-phenyleneoxide, abbreviated as PPO (see Fig. 5.8). Both the excellent catalytic activity and the specificity of the latter complex could be explained in sections III.4 and III.5 by the complexation ability of substrate anions in the copper-copper bridge positions of this binuclear complex. In particular, the formation of coordinated phenoxonium cations was enhanced by the improved possibility of a two-electron transfer process. The C-O coupling process was promoted by the reaction of these coordinated phenoxonium ions with substrate molecules or anions from the solution. Consequently, an efficient polymer production was observed.

The practical application of the oxidative coupling of terminal acetylenes proved to be rather discouraging due to the moisture-sensitivity of both applied macromolecular catalysts (compare sections IV.1 and IV.2) in the presence of this type of substrate. For this reason, the reaction mixture had to be continuously dried to prevent decomposition of the catalyst, since water is one of the reaction products (see Fig. 3.8.a). The stabilization capability of an excess of low molecular weight amine implied an undesirable competition with the macromolecular ligands as indicated in section IV.1.2.

The utilization of copper complexes with polyethylenimine derivatives was found to be unsuccessful even in the oxidative coupling of phenols, probably due to a combination of increased steric obstructions and excessive local concentrations (section III.6). Unfortunately, the introduction of pendant bidentates by chemical modification in order to achieve a lower local concentration of similar TMED-like ligands was also found to be unsuccessful because of undesired cross-linking side reactions (see section II.1.1).

Nevertheless, macromolecular copper complexes, similar to the copper/TMED counterpart in nature and catalytic behaviour, could be derived from copolymers of styrene and 4-vinylpyridine or N-vinylimidazole (see Tables 2.B and 2.C). The influences of the polymer chain on the catalytic behaviour of the attached sites were described in sections V.3 and VI.3. They were indicated by the dissimilar catalytic activities observed at different degrees of functionalization (Table 5.A). These different activities per copper ion must be ascribed to *local* effects, in particular to steric influences of the polymer chain on the rate-determining electron transfer process, since all overall concentrations were kept constant (see section V.3.1). Model studies, utilizing modified space-filling molecule models, reveal the steric interaction between a bridge-coordinated substrate anion and an intermediate chain segment linking both copper ions in the same binuclear complex (Fig. 5.8). It appeared that this interaction increased with decreasing segment length, i.e. with an increasing degree of functionalization, α. Consequently, the steric advantages of the tetrahedron-like transition state over the origional square planar state escalate with α, which accounts for the observed increase in reaction rate with decreasing intermediate segment length (section V.3.1).

The resulting increase in initial reaction rate with α is limited by abrupt reductions observed at distinct α values, which were explained in section V.3.2 by restrictions in the complexation ability in the macromolecular copper/amine/substrate complexes. In particular, model studies reveal the requirement of a minimum number of intermediate styrene units to afford the statistically most probable complexation of two neighbouring amines ("chelate effect"). Therefore, skipping of an adjacent amine in favour of the next-neighbouring one must occur on exceeding these crucial α values (Fig. 5.9). Consequently, the corresponding abrupt increase in intermediate chain length caused a decline in steric interaction with the coordinated substrate, accompanied by the observed steep fall in reaction rate. The similarity in α-dependency of both applied copper/styrene copolymer complexes, i.e. copper complexes with at-polystyrene-co-4-vinylpyridine and -co-N-vinylimidazole (see Figs. 5.10 and 6.3, respectively), supported this proposed mechanism.

The effect of chemical cross-linking of these macromolecular catalysts is described in section V.5. It appeared that this lowered their catalytic activity, since the accessibility of the catalytic centres is restricted by the attached extra chain branches. This limitation of local diffusion rates in the direct vicinity of the bridge coordination sites is even enhanced with α, due to an increasing local segment concentration (Fig.5.18).

The macromolecular imidazole catalysts proved to be more stable against a slight excess of mineral base than the pyridine counterparts. This advantage permitted partial titration of the substrate in order to enhance the concentration of phenolate anions. Section VI.4 describes the resulting enhanced bridge substitution and two-electron transfer process, successively. The subsequent reaction of phenolate anions with coordinated phenoxonium cations caused an enhanced C-O-coupled dimer formation at the expense of C-C-coupled dimers, which accounts for the suppression of DPQ

formation during the initial stages of the reaction. Moreover, the exclusive C-O coupling promotes the further grow of the C-O-coupled dimer to the polymer, PPO. This improved specificity behaviour of the present macromolecular catalyst could be optimized by raising the amine/copper or methanol/1,2-dichlorobenzene ratios in the reaction mixture. An almost exclusive production of the polymer product, poly-2,6-dimethylphenyleneoxide, may then be obtained.

SAMENVATTING

Deze dissertatie bevat een onderzoek naar de toepassing van polymeergebonden katalytisch aktieve plaatsen als geïmmobiliseerde centra voor homogene redox-katalyse. Een uiterst interessant aspect vormt hierbij het vermogen van de polymeerketen zelf om het katalytisch gedrag van de daaraan gehechte aktieve plaatsen te beïnvloeden, in plaats van slechts als een inerte drager daarvan te dienen (§ I.1, I.2 en I.3). Een gedetailleerde beschouwing van deze effecten vormt dan ook de kern van dit proefschrift (zie hoofdstukken V en VI).

Een optimale immobilisatie zou men bereiken door het gebruik van lineaire makromolekulen, welke met de eindstandige monomeerrest aan een inerte vaste drager zijn verbonden (Fig. 1.1). Op deze wijze kan het homogene karakter op lokale schaal gewaarborgd worden. Kinetische experimenten zijn thans nog uitsluitend uitgevoerd met oplosbare lineaire makromolekulen, waarvan de lokale aanpasbaarheid even optimaal is.

Oxidatieve koppelingsreakties, gekatalyseerd door koperkomplexen met polymeer-gebonden amines, bleken geschikte model-systemen om de makromolekulaire katalyse te onderzoeken (§ II.3). Daar één der modelreakties, de oxidatieve koppeling van 2,6-dimethylfenol, aanleiding gaf tot de vorming van verschillende produkten zoals is weergegeven in Fig. 2.6, waren ook de specificiteitseffekten te onderzoeken.

Makromolekulaire amineliganden zijn gesynthetiseerd door modifikatie van niet-funktionele polymeren (§ II.1.1) of door (co-)polymerisatie van funktionele monomeren (§ II.1.2). De laatste methode bood de voordelen van een betere regulering van de funktionalisatiegraad α en de ongevoeligheid voor vernettings-nevenreakties. De bereiding van makromolekulaire liganden over het gehele α-trajekt wordt hierdoor mogelijk gemaakt.

De aard van de katalytisch aktieve plaatsen zijn onderzocht in hoofdstuk III aan een geschikt laagmolekulair modelkomplex, een koperkomplex met het bidentaat N,N,N',N'-tetramethylethaan-1,2-diamine (TMED), n.l. $\{TMED.Cu(OH)_2Cu.TMED\}Cl_2$, waarbij gebruik is gemaakt van röntgendiffraktie (§ III.2), spektroskopische technieken (§ III.3) en kinetische experimenten (§ III.4). Er bleken twee verschillende binucleaire koper/TMED-komplexen te kunnen ontstaan, afhankelijk van de toegepaste bereidingswijze zoals aangegeven in Fig. 3.1. Het chloor-gebrugde komplex bleek slechts zwak aktief en veroorzaakte specifiek de vorming van het C-C-gekoppelde dimere produkt bij de oxidatieve koppeling van 2,6-dimethylfenol, n.l. het zogenaamde "difenochinon" (afgekort: DPQ). Daarentegen bleek het hydroxo-gebrugde komplex veel aktiever, waarbij hoofdzakelijk het polymere produkt poly-2,6-dimethylfenyleen-oxide (PPO) werd gevormd (zie Fig. 3.8). Zowel de uitstekende katalytische aktiviteit als de specificiteit konde verklaard worden in § III.4 en III.5 met de komplexatie-mogelijkheid van substraatanionen in de koper-koper-brugposities van dit binucleaire komplex. De vorming van gekoördineerde fenoxonium-kationen werd namenlijk verhoogd door de betere mogelijkheid van een twee-elektronen-overdracht. De reaktie

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